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Model-based approach to account for the variation of primary VOC emissions over time in the identification of indoor VOC sources

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ABSTRACT

The study objectives were to improve the understanding of the long-term variation of VOC emission chromatograms of building materials and to develop a method to account for this variation in the identification of individual sources of VOC emissions. This is of importance for the application of the source identification method since materials age over time in real indoor environments. The method is based on the mixed air sample measurements containing pollutants from *multiple aged* materials and the emission signatures of *individual new* materials determined by PTR-MS. Three emission decay source models were employed and evaluated for their ability to track the change of individual material emission signatures by PTR-MS over a nine-month period. Nine building material specimens were studied in a ventilated 50-L small-size chamber for their emissions individually for nine months, and also in combination later. Chamber exhaust air was sampled by PTR-MS to construct a temporal profile of emission signature unique to individual product type. The similar process was taken to measure mixture emissions from multiple materials, which is for applying and validating the developed method for source identification enhancement, considering the variation in long-term emission rates of individual VOCs. Results showed that the proposed approach could predict the emission signatures of individual building materials at a later time (9-month) with less than 6% difference variance, and hence indicated the potential of the source identification method for aged materials in real indoor environments.

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1. Introduction

Volatile organic compounds (VOCs) have multiple indoor sources. VOC emitting materials can introduce carcinogens, chemical mutagens, endocrine disruptors, neurotoxins, reproductive toxins and other harmful chemicals into indoor air. Besides, many VOCs are odorous compounds that may affect the perceived air quality in negative ways [1]. Such emissions should be minimized to reduce people's exposure and associated health risks and to improve human comfort. VOCs from indoor building materials include primary and secondary emissions. The primary emission is related to VOCs released directly from the materials into indoor air. The level of this emission is typically high immediately following the

application or introduction of a building product in indoor environments, and decays over a long period. This emission is a direct result of chemical constituents from the materials. On the other hand, the secondary VOC emission can occur when other indoor materials adsorb VOCs in the air, which are either emitted by other materials or generated from ozone-initiated chemical reactions [1,2].

As Hodgson et al. [3] indicated in their paper, source reduction by substituting building products with low-polluting materials or by modifying building practices could be the best preferred way for solving occupants' exposure problems to VOCs. They also reported several compounds including acetic acid, hexanal and nonanal as important indoor species having great potency to human's odor perception and health. However, they could not point out the origin of the measured active compounds in the tested houses. There is therefore an urgent need to identify and clearly point out VOC emission sources for establishing an effective remediation of unwanted VOC emissions. If any VOC problem is found in indoor

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environments, an effective solution may be to identify different potential/relevant sources by an online analytical monitoring device (e.g. Proton transfer reaction-mass spectrometry, or PTR-MS), which enables the recognition of relevant sources by comparing with a library containing a series of emission data of previously screened individual sources. Finding the source(s) would be the key step to eliminating the problem effectively. An advantage of this approach is that it may pinpoint the sources otherwise difficult to find when a building has an indoor air quality problem.

Variations with respect to concentrations and chemical compositions in the long-term VOC emissions have been observed and modeled in previous studies [4–7], which can impact the effectiveness of source identification [8–10]. Under controlled laboratory conditions, Han et al. [11,12] showed the existence of stable and unique emission signatures (ES) for different types of building materials (relatively new ones), and developed a methodology for separating and identifying the individual material emission signatures from emissions of multiple materials. However, to apply the identification methodology in practice under real field conditions, the emission decay characteristics of building materials have to be considered. The objectives of this study were to investigate the possible variations of primary VOC emission signatures over a long period and to develop a methodology to account for such variations in the identification of individual indoor emission sources based on mixed air sample measurements and the initial emission signatures of individual building products established by PTR-MS.

2. Materials and methods

2.1. Overview

In a previous study, chamber air polluted by nine typical building materials in a ventilated 50-L small-sized chamber was individually sampled by PTR-MS via the exhaust line at the different airflow rates of low, medium and high levels to construct an initial database of material emission signatures [11]. The emission signatures were found to be stable under different sampling time and different area-specific ventilation rates in terms of relative signal intensities and overall shape of emission mass spectra when the sampling was performed within a short period of time (less than two weeks). The emission signature is the PTR-MS ion mass (m/z) spectrum of the air polluted by the emissions of each material product. This feature of material emission signature can be established by subtracting the background air effect and by removing any ion mass components under the measurement uncertainty (<3 standard deviation of the background signal). In the present study, emissions of all VOCs comprising the ES for each material were measured over a long-term period (i.e. 9 months). Source models were evaluated for their ability to predict the long-term emission rates of individual VOCs, and hence the variation of emission signature for each material over time. Using the selected source models, the emission signatures of individual materials were estimated or predicted for the time point of emission source identification. Actual combined emissions from three multi-material mixtures were measured to determine if the approach would enhance the ES separation and identification performance of the source identification method previously developed [12].

Three source models – a double-exponential decay model [13], a power-law decay model [14] and a mechanistic diffusion model [4] – were applied to collected long-term and short-term (≤ 28 days) measurements for estimating and predicting the long-term VOC emissions and the corresponding material ESs for a given later period. The corresponding source identification performance

was then assessed by using three performance indices (to be defined in a later section).

2.2. Environmental chamber conditions

For both single and multiple material tests, a 50-L small-sized environmental chamber (whose dimension is $0.5\text{ m} \times 0.4\text{ m} \times 0.25\text{ m}$ high) finished with electro-polished stainless steel was utilized with a precise airflow controller and a humidity controller. The chamber conditions were controlled at a constant temperature in the range of $19.9\text{--}26.0\text{ }^{\circ}\text{C}$ (with a small variation of $<\pm 0.02\text{ }^{\circ}\text{C}$ during each sampling period) and at a controlled relative humidity of $31 \pm 0.3\%$ RH during the 9-month period of the experiment. Before each long-term test, the inner surface of the empty chamber was scrubbed with a paper towel which was saturated with isopropanol and DI water (SATPAX 1000, pre-saturated non-woven polyester/cellulose wipers). After that, the test chamber was ventilated for at least 24 h with clean filtered air at 2 ACH. In this way, the background concentration level of each measurable VOC in the empty chamber was maintained clean to be $<1\text{ }\mu\text{g m}^{-3}$.

2.3. Test specimens

Nine typical building materials were studied, including carpet, ceiling material, gypsum board, linoleum, paint 1 (water-based acrylic), paint 2 (with linseed oil), polyolefine, PVC and wood. The detailed descriptions for the specimens can be found elsewhere [11]. Each material sample was cut and prepared as specified in Table 1. Most of the studied materials except for Gypsum, Paint 1 and 2 were stapled back to back together in order that both sides of each specimen were exposed to the air in the test chamber, and a VOC-free aluminum tape (3M 2113) was applied to seal all edges. For Paints 1 and 2, both sides were painted and gypsum boards were used as their substrates. The prepared samples were then placed in a vertical way, parallel with the airflow direction in the chamber. The area-specific ventilation rate was adjusted by controlling the airflow in the chamber while the size of specimen kept unchanged. For testing the emissions from multiple materials, Carpet, Linoleum, Paint 2 (with linseed oil) and Wood were selected and used, which were the same materials utilized for the individual single material long-term tests.

2.4. PTR-MS setting

A high-sensitivity PTR-MS model (Ionicon Analytik with a detection limit as low as 1 pptv, Austria) was utilized for this study. The operating conditions were as follows: under the standard conditions (Drift tube pressure: $2.20 \pm 1.9\text{e-}5$ mbar, PC: 355 mbar, FC: 7.0 STP cc/min, U SO: 85 V, U S: 120 V, Drift tube voltage: 600 V and Source: 6.0 mA). PTR-MS was developed to overcome the drawbacks of GC methods, allowing online measurements of individual species at trace levels (down to ppb or even ppt level for some VOCs). In PTR-MS, the sampled air is continuously pumped into a drift tube reactor, and a fraction of VOCs is ionized in proton transfer reactions with hydronium ions (H_3O^+) as a chemical reagent. The benefit of utilizing proton transfer is that it can lead to soft ionization, generally not resulting in the fragmentation of product ions. At the terminal of the drift tube, a quadrupole mass spectrometer measures the reagent and product ions, and the product ion signal becomes proportional to the VOC concentration sampled. PTR-MS can monitor numerous VOCs of interest with a high sensitivity and a rapid response time for sampling (<100 ms). The general detection limits of the device are within 10–100 pptv. In addition, this technique does not require any sample pre-treatment such as drying or pre-concentration, and

Table 1

Flow rates and specimen areas for the PTR-MS experiments.

Material (ID#)	Flow rate – Q_v (l/min)/specimen area – A (cm ²) Q_v/A [m ³ /(m ² h)]					
	Meas. #1	Meas. #2	Meas. #3	Meas. #4 (mix)	Meas. #5 (mix)	Meas. #6 (mix)
Ceiling (3)	0.50/290.7 1.03	1.55/290.7 3.20	4.64/290.7 9.58			
Wood (9)	0.50/265.5 1.13	1.30/265.5 2.94	3.85/265.5 8.70	1.21/265.5 2.73		1.28/265.5 2.89
Carpet (7)	0.50/240 1.25	1.28/240 3.20	3.83/240 9.58		1.28/240 3.20	
Linoleum (8)	0.50/240 1.25	1.28/240 3.20	3.83/240 9.58	1.21/240 3.03	1.28/240 3.20	1.28/240 3.20
PVC (2)	0.50/240 1.25	1.28/240 3.20	3.83/240 9.58			
Polyolefine (1)	0.50/240 1.25	1.28/240 3.20	3.83/240 9.58			
Gypsum (4)	0.50/416 0.72	1.03/416 1.49	3.08/416 4.44			
Paint 1 (5)	0.50/402 0.75	0.99/402 1.48	2.97/402 4.43			
Paint 2 (6)	0.50/490.2 0.61	1.21/490.2 1.48	3.63/490.2 4.44	1.21/490.2 1.48		

Meas. stands for 'Measurement'.

Measurements #1–3: for single material long-term tests performed for 9 months to track the long-term VOC emission profiles and the corresponding change of material emission signatures.

Measurements #4–6: for material mixture tests performed right after the 9-month long-term tests to check the validity of the consideration of long-term emissions for the enhancement of source identification.

is thus well suited for oxygenated VOCs, which cannot be quantified from canister samples used in a traditional chemical analysis approach. Lindinger et al. [15] provides more detailed explanations on the device and its principle. The normalized product ion count rate (ncps) was generally utilized in the literature, so was it in the present study to quantify target VOC concentrations.

2.5. Test procedure and schedule

Previously, the nine typical building materials selected were studied at different area-specific ventilation rates (low, medium and high corresponding Measurements #1, #2 and #3) to construct a library of initial emission signatures by PTR-MS unique to individual building product. After one year of the experiment for the establishment of the initial ES library, long-term emission experiments using the same nine building materials preserved in a well sealed and conditioned storage have been performed at the corresponding medium airflow rates of individual materials for nine months (Table 1). The ES measurements for the long-term experiments were collected at Day-0 to Day-28 (designated as Long-term 1 measurement, starting at around 2 h after the start of continuous ventilation), at 7-month (Long-term 2), 8-month (Long-term 3) and 9-month (Long-term 4), which are illustrated in Fig. 1. Right after the long-term experiments, combined emission measurements from three multi-material mixtures were collected (Measurements #4–#6) to obtain actual combined emission signals and to assess the effect of the long-term ES variation on the source identification performance of the algorithms developed in a previous study [12].

For each measurement, the ion mass spectra were measured by PTR-MS for the background emission signal (in the empty chamber) and the sample emission signal (with each prepared specimen inside the chamber). The PTR-MS measurements started to be collected all after three volumetric air changes from the starting point of ventilation to obtain 95% of the quasi-steady state level. PTR-MS scanned from $m/z = 21$ to $m/z = 250$ per every 12 s with a 50 ms ion mass resolution interval. The overall sampling period for each dataset was 600 s to collect 50 ion mass spectra. A duplicate mass spectrum was also collected to verify the measured data during each measurement.

3. Results and discussion

The previous study [11] determined the specificity and identification of each ion mass with a related VOC by using GC/MS and PTR-MS together. Each ion mass of PTR-MS represents a VOC. Although some fragments are possible, the present study focused on the contribution of the dominant VOC to each ion mass. The signal intensity (ncps) of each ion mass now indicates the corresponding concentration level of the VOC. The emission signatures collected at Measurement #2 (medium airflow rate) was used as a reference in this study (See Table 1), and the variance of the emission signature for a given material was determined based on the variations of all the scanned ion mass peaks from the reference signature for the material.

3.1. Emission patterns in each long-term period

3.1.1. 2-Day (D-0 to D-2) emission profile (from long-term 1)

PTR-MS raw signals were filtered to effectively remove PTR-MS measurement noise by utilizing a moving-average method [16] with 11 samples (corresponding to the sampling period of 120 s) for each measuring point as conducted previously by Han et al. [11],

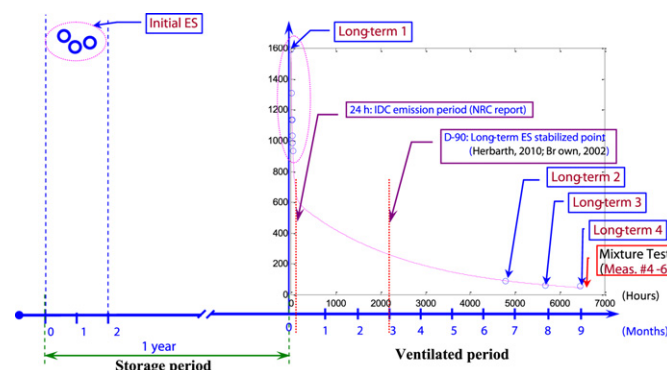


Fig. 1. Measurement schedule for constructing 9-month long-term emission signatures. ES: emission signature; and IDC: internal diffusion-controlled.

where the detailed descriptions on the filtering technique used can be found. Fig. 2 exemplifies the raw and filtered signal patterns for several major compounds from Paint 2 having higher concentration levels over a 2-day emission period. Contrary to the raw signal patterns for the major ion masses of Paint 2 ($m/z = 41, 43, 61$), the filtered signals exhibited clear trends of fast exponential decay over time. The concentrations of the background air components (e.g. $m/z = 29$) showed almost no change during this period of the emission experiment.

Among many compounds measured, most of the major VOC emissions from Paint 2 showed fast exponential decay profiles, especially for isopropanol ($m/z = 41, 43, 39$); Note: this specificity of these ion masses is a case-specific applied for the studied materials, so different compounds such as acetyl, aldehydes and propyl compounds can be detected at these ion masses for some other cases) and methanol ($m/z = 33$). The half-life time constant τ (which is the time for the emission rate to be reduced to 50% of its initial value) for these ion masses was less than 7 h. Actually, more than 70% of initial concentrations decayed after two days for this kind of compound. Still, several compounds such as acetic acid ($m/z = 61$) and ethanol ($m/z = 47$) showed a slower decay over time (its half-life time constant $\tau > 30$ h) than those fast decaying compounds ($\tau < 7$ h), which led to a huge effect on the shape change of the emission signature for Paint 2 at a later time. The emission signature for Paint 2 even at the end of this 2-day period had a quite different shape compared with the initial emission signature, or the reference emission signature for this material (Note: Some materials such as Linoleum and Wood having a steady emission decay over time for their major compounds showed almost no change in their emission signatures during the 2-day period. The half-life time constant τ of most major compounds for these materials was > 40 h, but the shortest one had the half-life of ~ 18 h. For this kind of fast decaying case, the profile change of material emission signatures for a long time may be accounted for by wisely utilizing appropriate emission source models [12,17,18]. This issue will be addressed in a later section.

3.1.2. ESs at 7-month (Long-term 2), 8-month (Long-term 3) and 9-month (Long-term 4)

The emission signatures for the building materials investigated in this study were found to change over time. However, the long-term emission signatures for these materials appeared to be stabilized again after a certain period of time (~ 3 months or 90 days, demonstrated by the emission profile in an average sense as shown in Herbarth and Matysik [19]) if the emission signal intensities by PTR-MS were high enough compared with those for the background air in the empty chamber (or having a high enough signal-to-noise ratio, SNR). The emission signature for a material consists of the collection of relative concentrations of all emitted VOCs measured. Depending on the dominance of relatively fast decaying compounds, the overall shape of the emission signature can be largely changed at an early stage of emissions. However, after the fast decaying compounds exponentially decay out after a certain time, the relative decay rates of the remaining compounds become similar (The emission rates linearly decrease over time gradually), making the emission signature stable after that time. The results of long-term emission signatures obtained during these periods (at 7–9 months) implied that there might be three types of materials in terms of the change of long-term emission signatures: Type 1 – materials with a single stable ES for a long time; Type 2 – materials with a stable initial ES and another stable ES for long-term emissions; and Type 3 – unstable long-term ES due to low SNR. The first type of material had its own stable emission signature from the early stage of emissions, and kept the similar shape of ES with a small variation in the ES until the end of the long-term emission experiment (up to 9 months in this study). An example of this material type was wood. Most of the materials belonged to the second type, which had a stable initial ES and another stable long-term ES appearing after a certain elapsed time. Examples of this type of material were Paint 2, Carpet and Linoleum. If materials themselves initially had a low-polluting property, the emission signals were measured at a very low level (or low SNR) and kept decreasing over time. After a certain period of time, the signals from

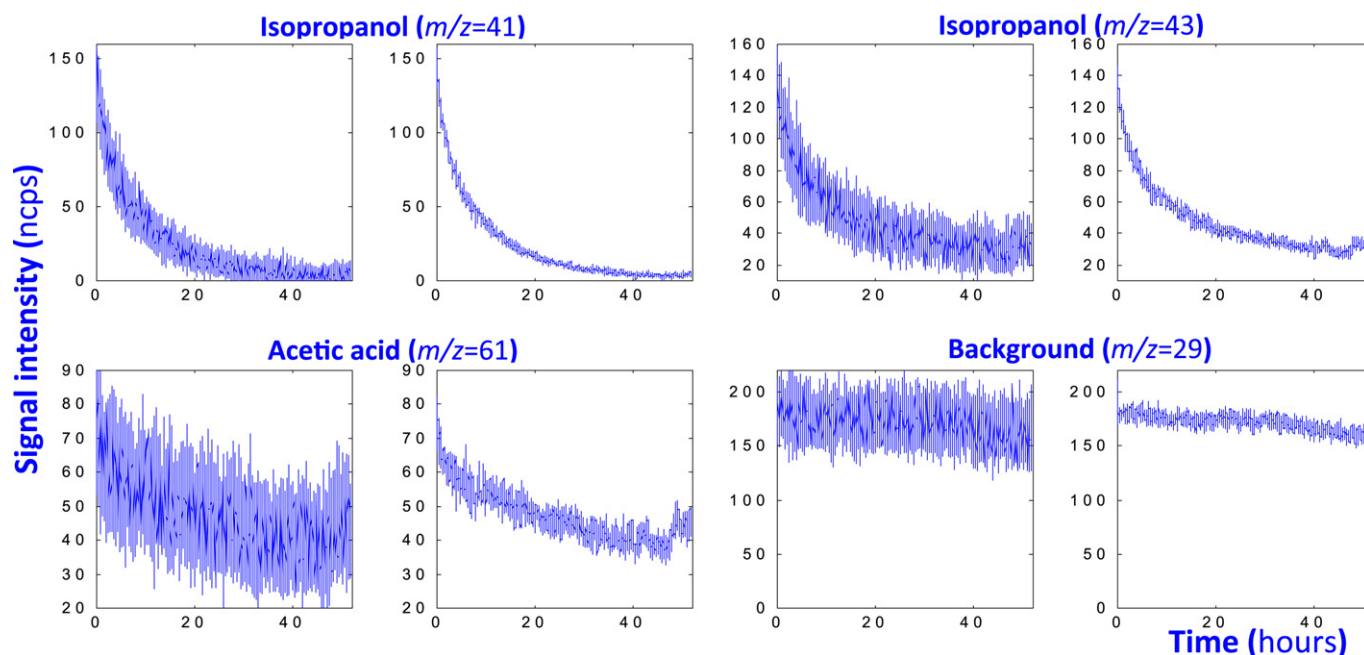


Fig. 2. PTR-MS raw vs. filtered emission signal patterns for several major ion masses of Paint 2. Each pair of figures represents the emission profiles of unfiltered (left of the pair) vs. filtered (right) signals for each compound presented.

these materials became far below the background signal level (i.e. <10 ncps, or 1.4 ppbv, whereas the level of the background air signals was around 50–60 ncps, or 7–8 ppbv), and the corresponding ESs could not be stable due to relatively high level of noise (or low SNR). All low-polluting materials in this study showed this trend including Polyolefine, PVC, Ceiling, Gypsum and Paint 1 classified as Type 3 (e.g. Fig. 4).

Fig. 3 exemplifies a case of Type 2 materials with Linoleum. The difference variance among the long-term ESs for Linoleum was less than 2% (when $m/z = 59$ was not considered) with regard to the maximum peak of the ES at 7 months (Long-term 2). Fig. 4 illustrates an example of Type 3 materials with Gypsum. Its signal intensities were all below 5 ncps (<1 ppbv), far lower than those of the background air signals (50–60 ncps, or 7–8 ppbv). Materials having the concentration level lower than 10 ncps might get susceptible to the background signal change and measurement noise, making it infeasible to obtain a stable signature. In this study, we are dealing with trace level of VOCs emitted from building materials, having tens of ppb level of concentrations, and this level became lower than even 1 ppb after the 9-month ventilation especially for low-polluting materials. For this case, it was hard for human subjects to detect the effects of VOCs from these low-polluting materials due to the low concentrations of the emitted compounds far lower than the detection limits of human sensory systems. Even though the ESs for low-polluting materials were found to be unstable in this study, it is not problematic as they do not contribute to pollution. If we deal with much higher concentration levels than the present ones even for Type 3 materials

classified in this study, a stable long-term ES for each case might be obtainable, considering that the stabilized trends for long-term ESs appeared to exist in other building materials and that these type 3 materials also had a stable initial ES for each case when the pollution level was relatively high enough at their early stage of emissions.

3.2. Long-term ES prediction/estimation by using source models

Can the long-term emission signatures for a later period of time be predicted or estimated by using some information on the initial material emission signatures? This section will challenge this question, providing feasible mathematical approaches (i.e. source models) to reach a solution and recommending a practical procedure for establishing a library of long-term emission signatures for future research on this topic.

The present study investigated the feasibility of the prediction and estimation of long-term emission signatures by using partial ES measurements at an early emission stage and source models. Two materials – Linoleum and Paint 2 – were selected and studied in this aspect, and their results are presented here as an example because these two materials are representative of two characteristic material types distinct by their steady (or slow) emission decay and fast emission decay over time, respectively. The measurements at $t_{\text{meas}} = [1, 14, 24, 29, 34, 39, 44 \text{ hours, Day 7, Day 14 and Day 28}]$ were sampled and utilized for this examination. Three source models – a double-exponential, a power-law decay models and Little's mechanistic diffusion model – were applied to get the

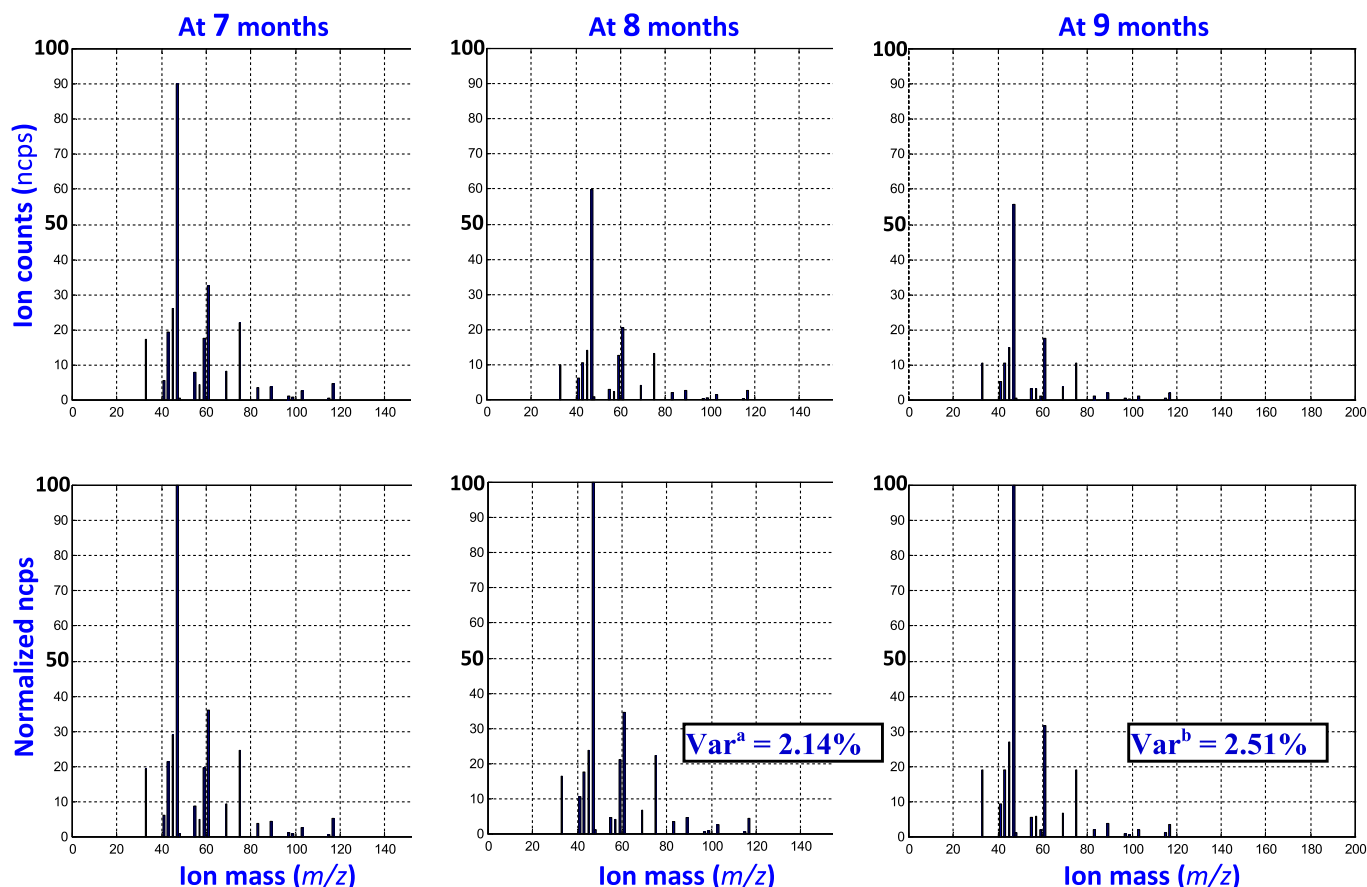


Fig. 3. Stable emission signatures for Linoleum after the 7-month long-term emissions. For two figures in each column, the figure on the top is a measured concentration profile along different compounds, and the bottom one is the normalized profile of the above, which is the emission signature of the material at the given sampling time. Superscript a indicates the difference variance between the ES at 7 months and that at 8 months when subtracting each other, expressed in percentage with regard to the maximum peak value of the ES at 7 months. Superscript b is the difference variance between the ES at 7 months and that at 9 months.

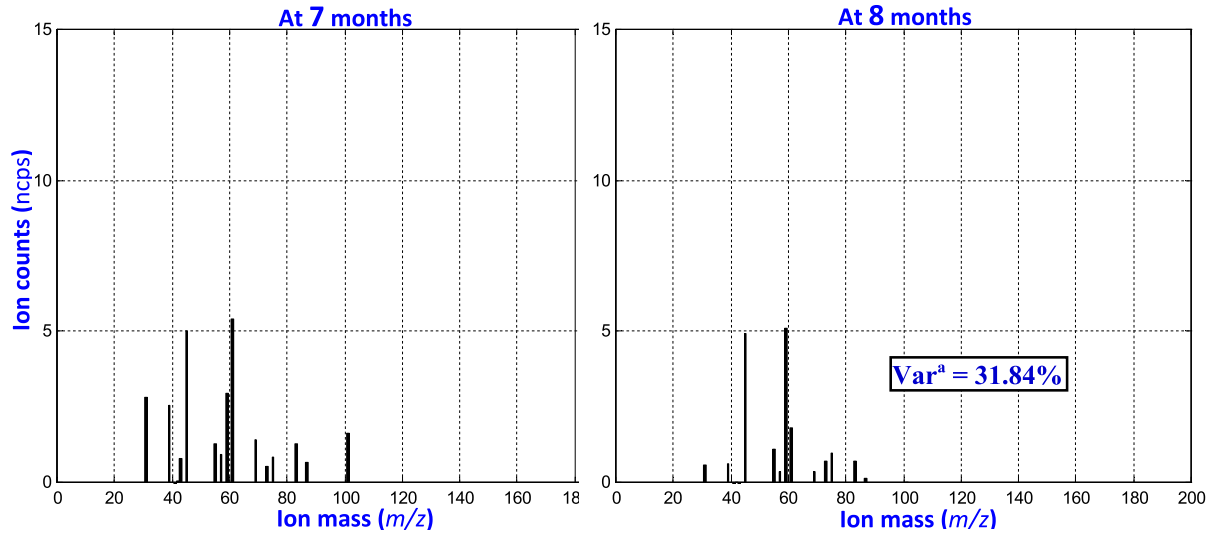


Fig. 4. Quite different emission signatures for Gypsum at 7 and 8 months due to its low signal-to-noise ratio (SNR). Superscript a represents the difference variance between the ES at 7 months and that at 8 months when subtracting each other, expressed in the percentage of the maximum peak value of the ES at 7 months.

optimal emission fitting line for each case in terms of least squared error between the estimated concentrations and the measured ones, by using Powell search algorithm [20] implemented via a Matlab toolbox. The fitting results were used for predicting the long-term emission rates and the corresponding ESs at 7, 8 and 9 months. The ES estimation is also possible using the full measurements collected for the period of 9 months. However, the estimation results were not presented here in detail due to the limited available pages, but were partially reflected in Tables 3 and 4. For the fitting with the power-law model, only the measurements after 24 h were used because of the apparent internal diffusion-controlled emissions observed after this hour (refer to Ref. [5] and the NRC report [14]).

3.2.1. A double-exponential decay model

Brown [13,21] used source models (i.e. first-order exponential and double-exponential decay models) in his study for exploring persistent low levels of VOC concentrations in established dwellings due to long-term emissions from building materials. First, in the present study, the double-exponential decay model (similar to that of Colombo et al. [22], having four control parameters to be determined) was applied to the long-term emission measurements, defined as follows:

$$EF = EF_0 \cdot \exp(-k_0 \cdot t) + EF_1 \cdot \exp(-k_1 \cdot t) \quad (1)$$

where EF represents the emission factor for source materials in the unit of $\mu\text{g m}^{-2} \text{h}^{-1}$, EF_0 is the initial emission factor of short-term emissions, EF_1 that of long-term emissions ($\mu\text{g m}^{-2} \text{h}^{-1}$), k_0 and k_1 indicate the corresponding decay constants for the short-term and long-term emissions, respectively (h^{-1}), and t is the elapsed ventilation time (h).

3.2.2. A power-law decay model

Second, the power-law decay model [14] was applied to the long-term emission measurements, defined as follows:

$$EF = a \times t^{-b} \quad (2)$$

where EF represents the emission factor for source materials in the unit of $\mu\text{g m}^{-2} \text{h}^{-1}$, a and b are empirical constants which are the control parameters to be determined for this model, and t is the elapsed ventilation time (h).

3.2.3. A mechanistic diffusion model

Third, a simple physically based diffusion model, which assumes that all of the material emissions are coming from the constituents of materials, was utilized in the present study to evaluate the potential and advantages of this diffusion model approach for predicting the long-term VOC emissions and the corresponding emission signatures. The mechanistic diffusion model introduced in this study mainly considered internal diffusion-controlled emissions, not reflecting the convective mass transfer resistance adjacent to a material surface. However, this convective term should come into the consideration if the air velocity in the chamber becomes large. In addition, it should also be noted that the convective mass transfer coefficient is not a controlling factor for emissions from dry materials where the internal diffusion resistance is much larger than the convective mass transfer resistance. The detailed descriptions for the diffusion source model can be found elsewhere [4] and defined here as follows:

$$\partial C(x, t) / \partial t = D \cdot \partial^2 C(x, t) / \partial x^2 \quad (3)$$

where $C(x, t)$ denotes the concentration of a VOC measured in a studied building material in the unit of $\mu\text{g m}^{-3}$, D the diffusion coefficient ($\text{m}^2 \text{h}^{-1}$), x is the linear depth of the material from the bottom (m), and t is the elapsed ventilation time (h). The initial condition (IC) associated with the model assumes that the compound of interest is uniformly distributed throughout the material such as

$$C(x, t) = C_0 \text{ for } 0 \leq x \leq L \quad (4)$$

where L indicates the thickness of the material (m), and C_0 represents the initial concentration of the compound in the material ($\mu\text{g m}^{-3}$). The corresponding first flux boundary condition (BC) assumes that there is no flux out of the bottom of the material such as

$$\partial C(x, t) / \partial x|_{x=0} = 0 \quad (5)$$

The second flux boundary condition is formulated through a mass balance on the VOC in the chamber air such as

$$(V/A \cdot K_V) \cdot \partial C(x, t) / \partial t|_{x=L} + D \cdot \partial C(x, t) / \partial x|_{x=L} + (Q/A \cdot K_V) \cdot C(x, t)|_{x=L} = 0 \quad (6)$$

where V is the volume of air in the chamber (m^3), A the emitting surface area of the material, Q the volumetric ventilation rate of air ($\text{m}^3 \text{h}^{-1}$), and K_v represents the equilibrium partition coefficient.

Different from empirical methods (providing little insight on the controlling mechanism governing VOC source behaviors and, as a result, of little value when extrapolating to other environmental conditions not covered by the chamber experiments), a mechanistic diffusion model for indoor sources controlled by internal diffusion processes has great potential and considerable promise for predicting emission characteristics when compared with empirical models [23], because diffusion is one of the most important mechanisms governing VOC source emissions. The three control parameters of this source model (i.e. the initial concentration of VOC in a material C_0 , the equilibrium partition coefficient K_v and the diffusion coefficient D) for each case were determined from the iterating process using the Powell searching method [20], minimizing the least squared error between the estimated concentrations and the actual measurements at the given sampling time.

3.2.4. An example of the prediction of long-term emissions

Fig. 5 shows the prediction using the diffusion source model for one of the major compounds of each material case (i.e. ethanol from Linoleum and propanoic acid from Paint 2), comparing this approach with the two empirical source models (Note: for other compounds, a similar trend as that of the above figure was observed. The results in the figure were presented here as an example of this approach). The purple dotted, blue dotted and black solid lines represent the optimal concentration profiles when the short-term measurements are given, resulted from the double-exponential, power-law and diffusion models, respectively. The figure demonstrates that, because of measurement noise, the determination of sampling interval may affect the resulting trend of emission fitting line in a significant way, especially for the cases with low level of VOC concentrations (due to low SNR), which did happen many times in this study because of dealing with trace VOCs.

The double-exponential decay model seemed to fit the initial response of long-term emission profiles more adequately than the power-law model when the selected sampling schedule (≤ 28 days)

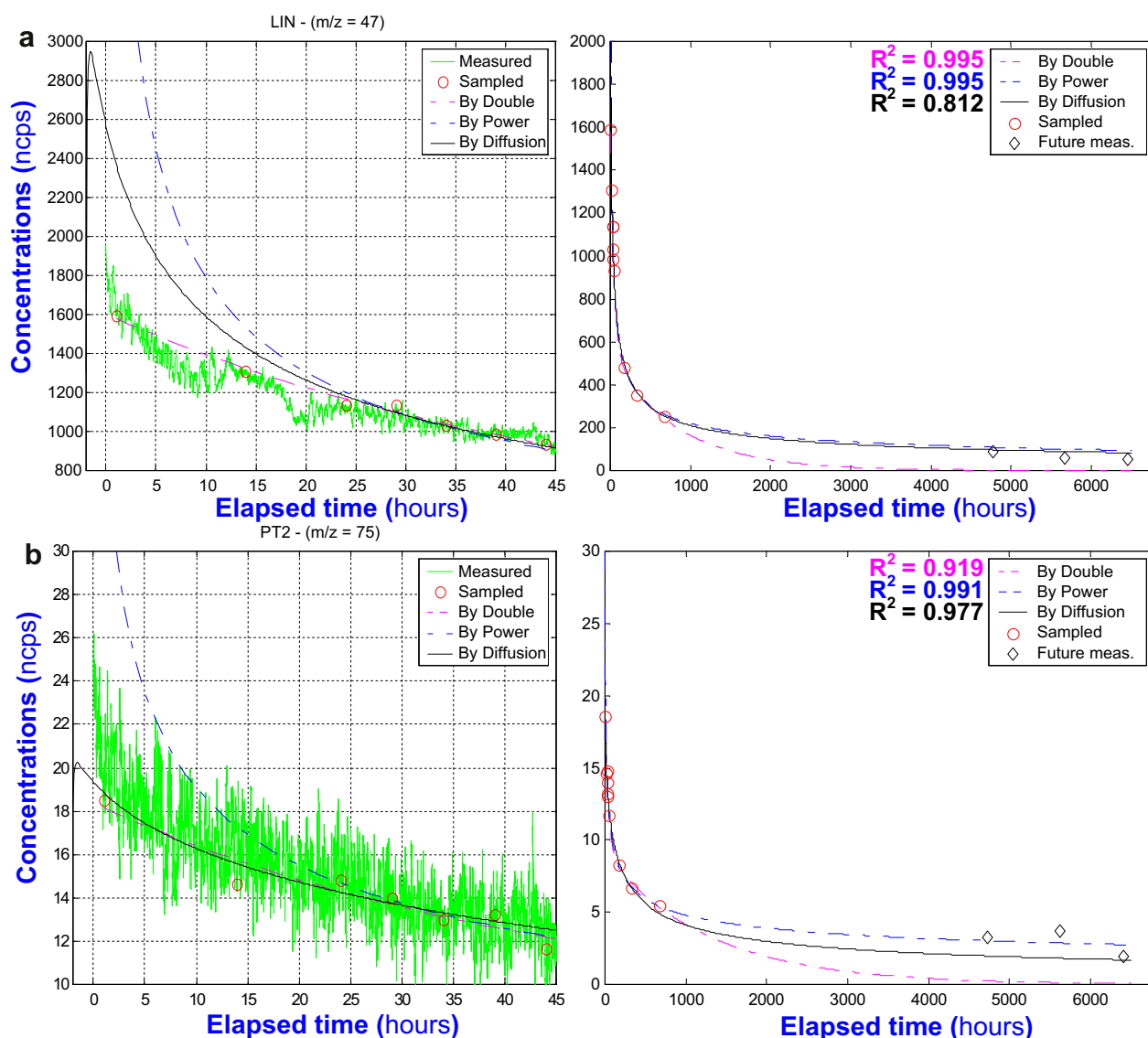


Fig. 5. Predictions of the long-term emissions at 7, 8 and 9 months by source models with short-term measurements (≤ 28 days). (a) Ethanol ($m/z = 47$) from Linoleum. (b) Propanoic acid (with a small portion of ethanol, $m/z = 75$) from Paint 2. 'Future meas.' represents the actual measurements obtained later at 7, 8 and 9 months for the comparison.

was utilized. The number of control parameters to be estimated for this model (4 parameters) is more than that of the power-law (2 parameters), which can make the fitting process of this model harder and more time-consuming (sometimes, infeasible) than the case with the power-law. In addition, the fitting results from this model appeared to become more mathematically oriented (finding the final solution best in terms of least squared error to the given measurements) than those of the power-law mainly due to the short-term measurements, not physically oriented.

On the other hand, the power-law decay model seemed to more properly represent the physical decay property of long-term VOC emissions, when samples only after 24 hours were used, for most of the cases investigated in this study than the double-exponential model. This is due to the observed fact that this source model was effective in representing the internal diffusion-controlled emissions of VOCs. Because of this attractive property of the source model reflecting the proper physical decay characteristics even with short-term measurements, the prediction of long-term emissions by the power-law model had lower errors than that from the double-exponential, which can be seen in Figs. 5–7, and is summarized in Table 2. This model showed a fast convergence and a high success rate in finding the final solution with a given tolerance level. Figs. 6 and 7 show the prediction trends for other major compounds from Linoleum by using the double-exponential and the power-law decay models, respectively.

The mechanistic diffusion model showed a better initial response than the power-law and a similar initial fitting

performance equivalent to the double-exponential. This model could show the up-and-down concentration change at an early stage of VOC emissions, well representing the behind physics of VOC emission characteristics as illustrated in Fig. 5. The long-term emission predictions at 7, 8 and 9 months were good and for some cases, better than those by the power-law. Like the case of the double-exponential decay model, the fitting process was hard and time-consuming (due to the use of partial differential equations), and even infeasible with a bad-conditioned initial guess of the model parameters. The good prediction property of this diffusion model for the entire emission period was highly encouraging because the model parameters could also be measured using procedures completely independent of the chamber studies and their measurements, or obtained from the comparison with expected values, where possible [4,23]. Because of this property, a shorter term of emission measurements than 28 days could be used to predict the long-term emission signatures for a longer period of VOC emissions.

Except for outliers, the mean percentage of prediction errors at the target months with the double-exponential model was <15% for Linoleum (>0.59 of R^2 , note: R^2 is calculated for all the points presented, which are the sampled measurements and the future measurements) and <19.1% for Paint 2 (>0.91 of R^2) when applied to all ES composing compounds of each material, whereas that with the power-law was <3.3% for Linoleum (>0.93 of R^2) and <4.1% for Paint 2 (>0.86 of R^2) as shown in Figs. 6 and 7 and Table 2. The absolute magnitude of this prediction error was calculated in

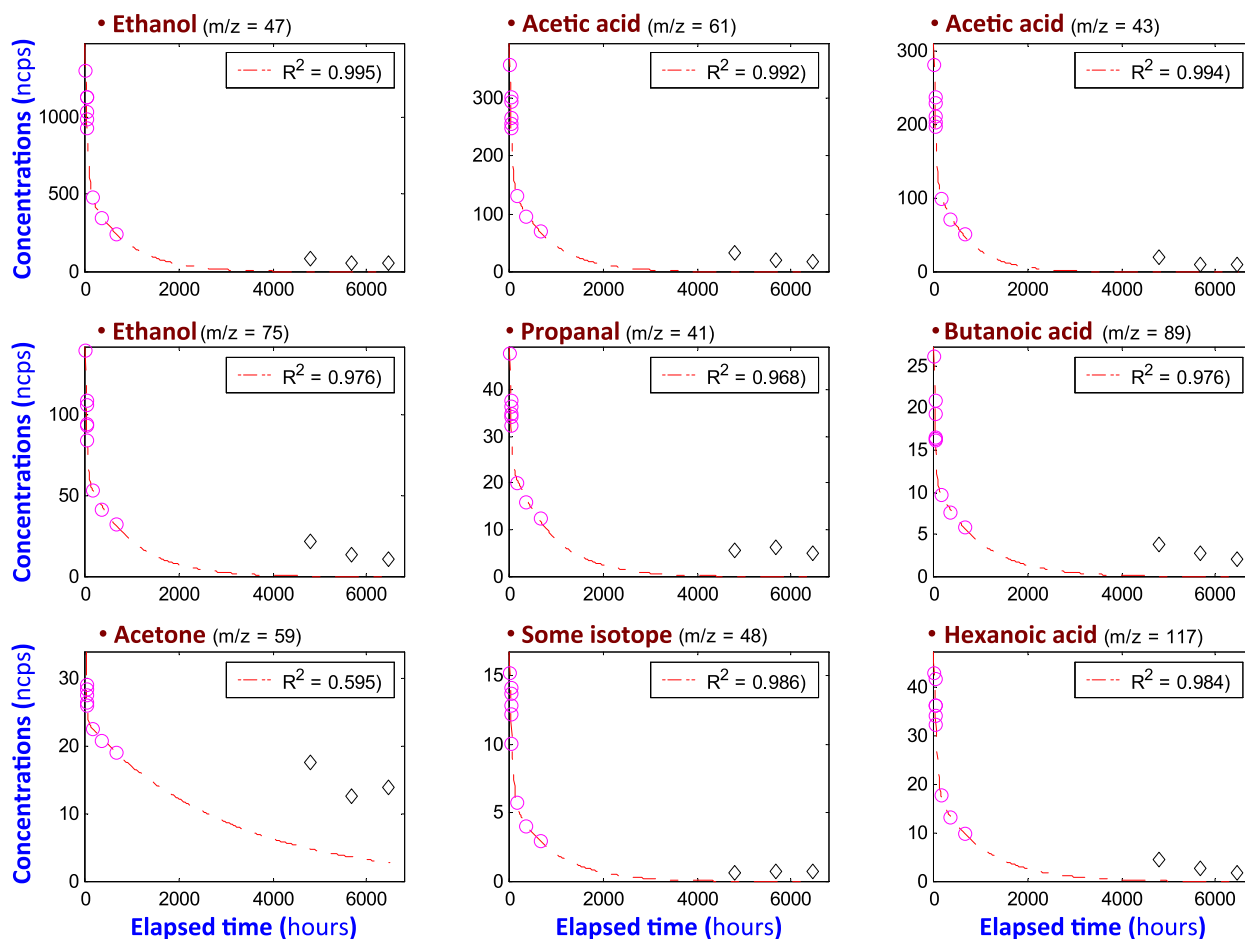


Fig. 6. Concentration predictions by the double-exponential decay model for selected compounds from Linoleum. The red dotted lines indicate the fits using the model, and the purple circles represent the actual measurements. R^2 or COD (coefficient of determination) is calculated for all the points presented – the sampled and future measurements (diamond dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

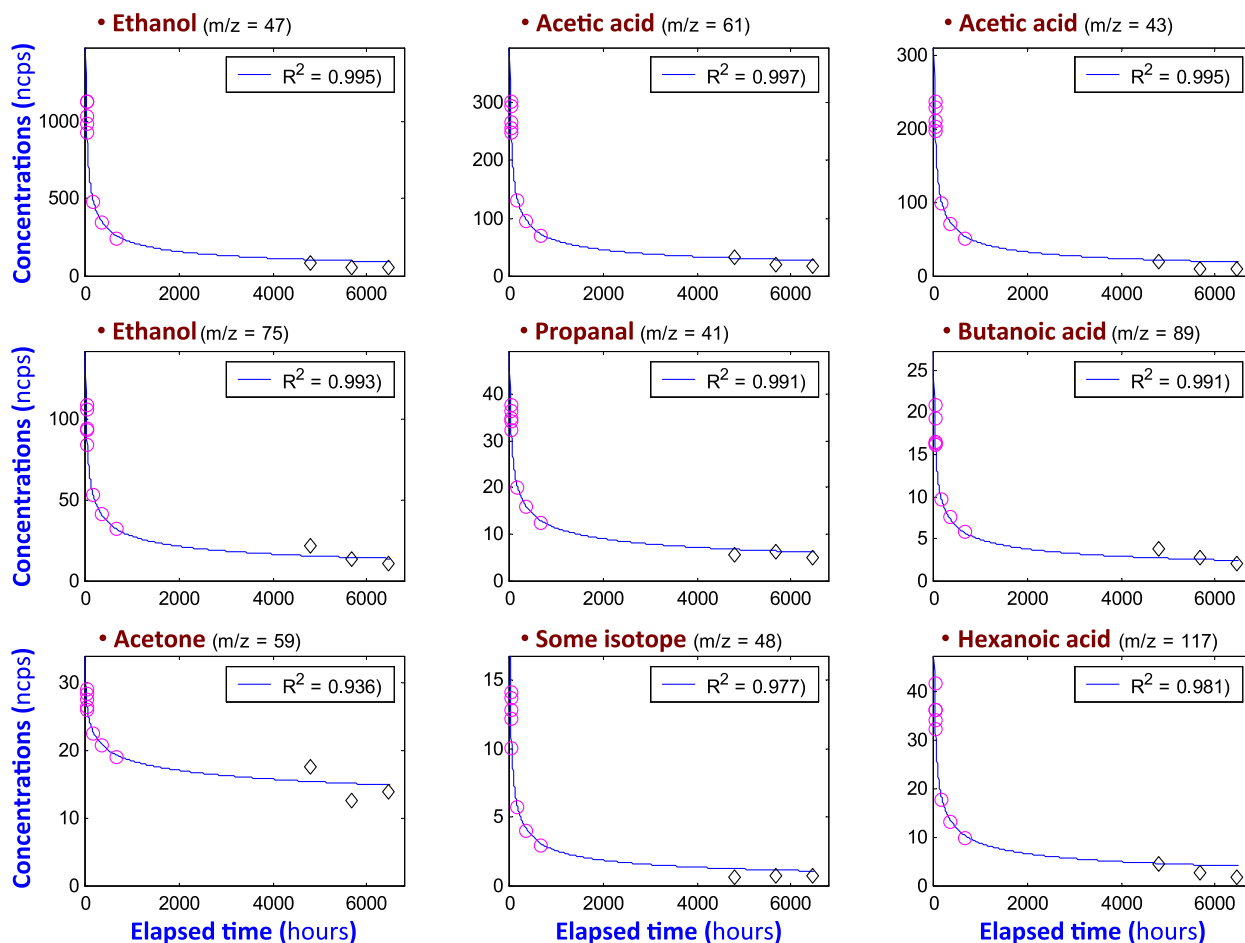


Fig. 7. Concentration predictions by the power-law decay model for selected compounds from Linoleum. The blue solid lines indicate the fits using the model, and the purple circles represent the actual measurements. R^2 or COD (coefficient of determination) is calculated for all the points presented – the sampled and future measurements (diamond dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

percentage with regard to the concentration level at 24 h in the profile of each case. Please note that the prediction results using the mechanistic diffusion model had a similar tendency to those of the power-law, so the details are not presented here.

3.2.5. Prediction of the corresponding long-term emission signatures

Long-term emission signatures can also be predicted at a certain given time by utilizing the source models. Fig. 8 exemplifies this

approach for the prediction of emission signatures and shows the performance result using a source model for Linoleum at the 9-month period (Note: the prediction from the mechanistic diffusion model had a similar performance error level to that of the power-law). The figure implies that, with some information on the measured profiles of material emission signatures over an early stage, the long-term change of ESs for a given material at a specific elapsed time can be effectively predicted and may be used for enhancing the performance of source identification. The prediction

Table 2

Summary of the emission prediction errors by two empirical source models (w/ 28-day measurements).

	Linoleum						Paint 2						
	7 months		8 months		9 months		7 months		8 months		9 months		
	Db	Pw	Db	Pw	Db	Pw	Db	Pw	Db	Pw	Db	Pw	
<i>m/z</i> = 47	7.55	1.52	5.07	3.36	4.75	3.23	10.65	0.77	16.31	5.83	10.54	0.47	<i>m/z</i> = 43
61	10.38	0.38	6.62	2.73	5.69	3.16							
43	7.78	1.21	4.27	4.06	4.31	3.55	14.49	3.20	16.21	0.90	12.92	3.63	61
75	18.99	5.75	11.48	1.38	9.18	3.21							
41	13.85	3.06	15.51	0.57	12.91	2.61	21.36	1.86	24.74	5.37	13.00	5.67	75
89	18.16	5.59	12.85	0.70	9.72	2.01							
59	41.61	7.79	29.35	8.69	36.48	3.18	24.64	4.42	46.76	17.46	28.80	4.18	57
48	4.71	3.98	5.56	2.65	5.11	2.66							
117	11.38	0.05	6.31	4.34	4.76	5.39							
Mean (%)	14.93	3.26	10.78	3.16	10.32	3.22	17.78	2.56	26.00	7.39	16.31	3.49	

Db: by the double-exponential decay model, Pw: by the power-law decay model. The bold values in the table are considered as outliers.

The presented values in the table are the absolute deviation percentage from the measurements, calculated by subtracting the predicted concentration from the actually measured one for each compound at the corresponding time and expressed in percentage with regard to the concentration level at 24 h of each corresponding concentration profile.

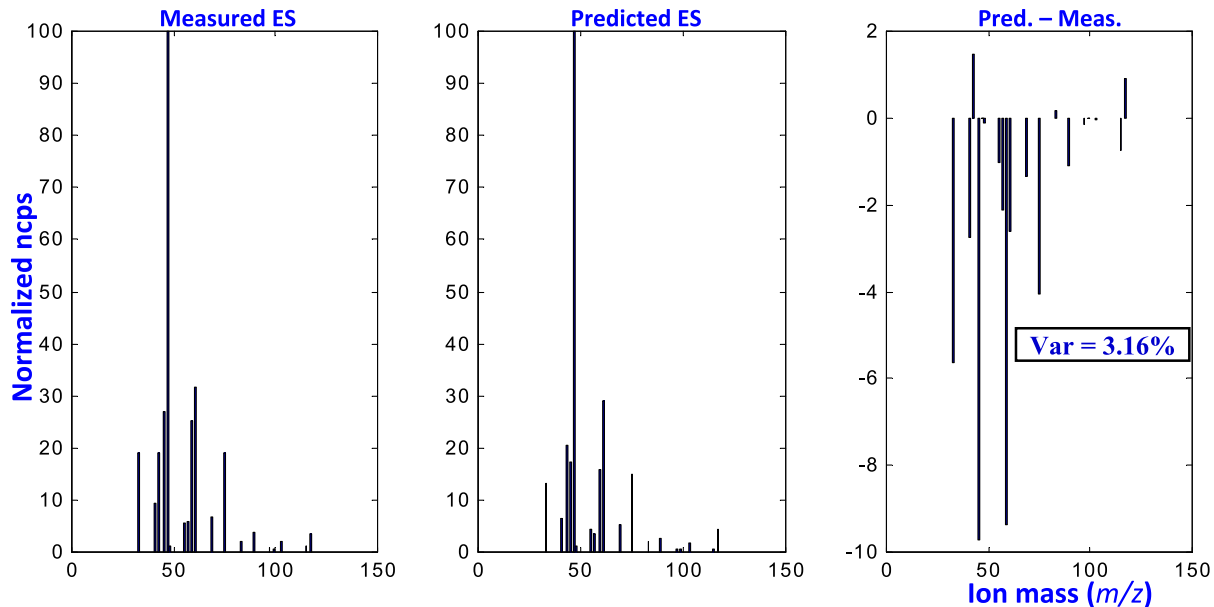


Fig. 8. Prediction of emission signatures exemplified with Linoleum at 9 months via the power-law decay model. 'Var' represents the difference variance between the predicted and measured emission signatures for the case.

performance of the long-term ES for Linoleum was 3.16% in terms of difference variance when the power-law decay model was utilized to predict it at the 9-month period with the 28-day short-term measurements (Note: The percentage value here represents the difference variance between the predicted emission signature and the measured one for a target material at a given time. The smaller the values, the better the ES prediction performance).

3.3. Source ID enhancement with the consideration of the long-term ES change

The mathematical approach described in the previous section for the prediction of emission signatures with the source models may improve the ES separation and identification over the course of long-term emissions. First, the dataset of ESs for a given set of materials can be established again at a specific elapsed time by considering the long-term emission change of all composing VOCs measured for each material under the given conditions and be used for enhancing the performance of ES separation and identification. By use of this prediction approach with a short-term emission dataset, the change of source identification performance can be assessed. Fig. 9 is the predicted library of ESs at the 9-month period by utilizing the power-law decay model (again, the mechanistic diffusion model had a similar tendency) and the 28-day short-term emission measurements. Actual combined emissions from three material mixtures (Measurements #4–6) were used to assess the source identification performance of two algorithms previously developed [12] when the ES library was predicted and reconstructed for a given period by use of the short-term emission dataset.

3.3.1. Reconstructed library of long-term ESs (at the 9-month period, using the power-law model)

Fig. 9 summarizes the reconstructed ES library at the target period of prediction.

3.3.2. Prediction errors of the ESs

Table 3 shows the ES prediction results when the power-law decay model was used with a 28-day short-term emission dataset. For comparison, the estimation results by the power-law with

the full long-term measurements are also presented in the table. There was only slight degradation in the ES prediction performance when a short-term emission dataset was utilized as shown in the table. Except for an outlier, the difference variances of the ES predictions were less than 6% (however, they were <5% when estimated).

3.3.3. Enhancement of the source identification performance

Right after the long-term experiment, at the 9-month period, the actual combined emissions from three material mixtures were measured under the environmental conditions defined in Table 1 (Measurements #4–6). For each mixture, 50 emission samples were measured by PTR-MS and processed by following the signal processing procedures described in the previous study [11] to get the corresponding emission signatures for the mixtures. The PTR-MS ESs measured for these combined emissions were applied to the two developed algorithms [12] with and without considering long-term ES change. The algorithms for source identification modeled the measured emission signature of a material mixture by PTR-MS as follows:

$$S_{sp}(x_n) = \sum_i [\alpha_i \cdot S_i(x_n) + w_i(x_n)] \text{ for } \forall x_n, \text{ with } \alpha_i > 0 \text{ for } \forall i, \\ n = 1, 2, \dots, M \quad (7)$$

where sp indicates 'the sample measured'; i is the material ID of the correct material set for the mixture, defined in the database of material emission signatures; $S_{sp}(x_n)$ represents the PTR-MS signal intensity of the measured sample for a given ion mass x_n (not normalized); $S_i(x_n)$, the normalized magnitude of emission signature for a given ion mass x_n of material i (it should be noted that an emission signature for each studied material is stored in the library in a normalized profile having the peak magnitude of 100 as its maximum); $w_i(x_n)$, the independent measurement noise for the ion mass x_n contained in the signal for material i ; and α_i is the signal intensity multiplication factor of the emission signature for material i . The first step of the developed algorithms is to scan the ion mass components in the measured sample emission signature by comparing with those in the library. Because of noise, several

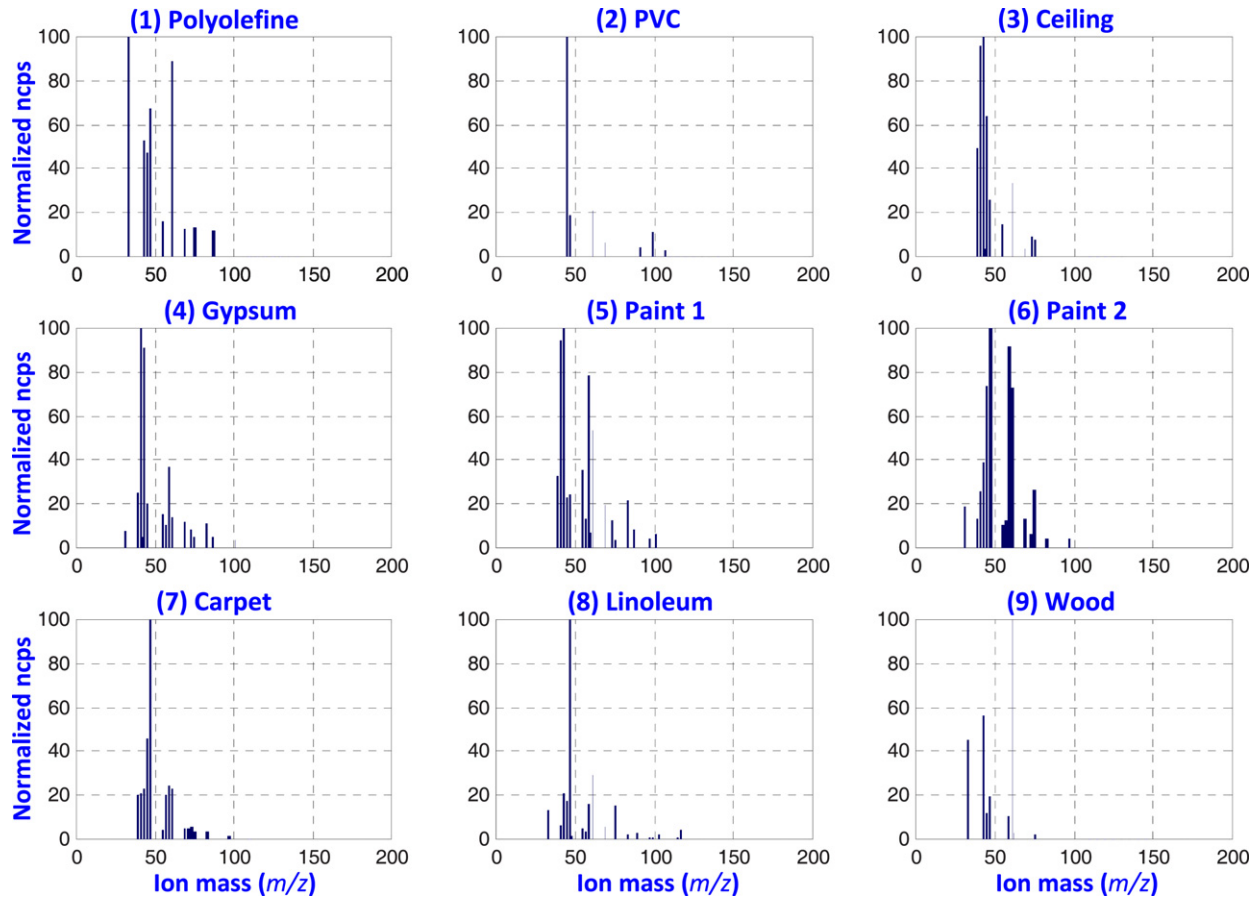


Fig. 9. Reconstructed library of emission signatures based on the predictions for the 9-month period (w/ 28-day short-term data). This library was predicted for the 9-month period by use of the power-law decay model with short-term emission measurements (≤ 28 days).

components may have small deviations from the exact values of ion masses. For this reason, the developed algorithms try to find any matching emission signatures in the library (a set of materials denoted as {db}), by utilizing a detection and estimation theory used for radar and electromagnetic wave transmission. The second step is to find the optimal set of signal intensity factors $\alpha = [\alpha_{ID1}, \dots, \alpha_{IDj}, \dots, \alpha_{db}]$ within the selected set of material emission signatures {db}, where ID_j indicates the j th material ID in the set of {db} selected as possible material candidates. Here, α_i s are unknowns to be estimated in an optimal sense while $S_{sp}(x_n)$ is measured by PTR-MS and $S_l(x_n)$ is given in the library for all scanned ion masses, where $n = 1, 2, \dots, M$. Algorithm 1 utilized the multiple regression least squared error (MRLS) between the measured emission signature of the mixture and the modeled one expressed as in Eq. (7) for this optimal process, and Algorithm 2 used a similar performance index with a normalization technique. More detailed descriptions for these algorithms can be found elsewhere [12].

The performance of ES separation and identification for each case was then assessed according to the performance indices – error norm expectation, success score expectation and success rate, defined as follows (the detailed definitions can be found in Han et al. [12]):

$$\text{Err} \equiv E\{\|\vec{\alpha}_{\text{est}} - \vec{\alpha}_{\text{true}}\|_2\}, \text{Score} \equiv E\{\text{scr}(N)\},$$

$$\text{SR} \equiv \left(\frac{N - N_{\text{fail}}}{N} \right) \times 100\% \quad (8)$$

where Err represents the expected value of the 2-norm of the difference between the estimated value of signal intensity factor vector ($\vec{\alpha}_{\text{est}}$) and the ground truth vector ($\vec{\alpha}_{\text{true}}$); N , the total number of identification trial samples collected for each mixture emission case (i.e. 50 samples in the present study), N_{fail} , the number of material identification failures that occurred (e.g. if every material in the sample is correctly identified with several wrong candidates, this case is classified as success. On the other

Table 3
Summary of the ES prediction errors by the power-law model (w/ 28-day measurements).

	Long-term 2 of LIN ^a (7-month)	Long-term 3 of LIN (8-month)	Long-term 4 of LIN (9-month)	Long-term 2 of PT2 ^a (7-month)	Long-term 3 of PT2 (8-month)	Long-term 4 of PT2 (9-month)
Power	3.91% ^b	2.85%	3.16%	4.92%	5.96%	6.87%
Its Est. ^c	3.29%	2.29%	2.54%	4.93%	4.66%	5.98%

^a LIN: linoleum, PT2: paint 2.

^b The percentage values in the table represent the difference variances between the estimated emission signatures and the measured ones at a given time. The smaller the values, the better the prediction performance.

^c The values in this row are the ES estimation results using the full long-term emission measurements, and presented here for the comparison purpose with the prediction results.

hand, if there is any missing material identified in the final set of the material candidates, then it is declared as failure. As an example, for [6 8 9], if the ID result is [1 3 6 8 9], this is considered as success. However, if the result is [5 6 8], this is failure); Score, the expected value of success score (scr) defined as: (if the ID result is success with exact identification, then $scr = 100$; if success with n wrong candidates, then $scr = 100 - 10 \times n$; and if failure, $scr = 0$); and SR is the success rate in material identification defined in percentage.

To compare the performance results, the ground truths for the correct material IDs were already given and the corresponding emission levels expressed by signal intensities were obtainable by separating each measured mixture signature in an optimal way by MRLS (as an example, the separation result of the measured signature for a mixture, Measurement #4, is shown in Fig. 10). 'Ground truth' value is the best estimate on, in this case, the material ID and its corresponding relative concentration level (i.e. signal intensity factor), which refer to information that is collected 'on location'. In remote sensing, this is especially important in order to relate image data to real features and materials on the ground, and to assess the performance and the error level. In the present study, this best estimate was drawn from the initial knowledge of the correct pair of materials and the best possible profile of emission signatures under the given environmental conditions. On the contrary, the two source identification algorithms know only the measured emission signature for each material mixture and the library of emission signatures established at an early emission stage. Measurement #4 (three-material mixture) was comprised of Paint 2 (Material ID = 6), Linoleum (ID = 8) and Wood (ID = 9). Both algorithms identified the correct sources of material emissions with some false materials: for Algorithm 1 with the initial library (INIT), Carpet (ID = 7), so success score (scr) = 90; for Algorithm 2 with the long-term library (LT), Ceiling (ID = 3), so success score (scr) = 90. In addition, the corresponding emission levels from each material of the mixture could be estimated by both algorithms with reasonably small errors (error expectations, or Err, were < 1.0 for both cases when the long-term library was used). The performance

results of the two algorithms for an actual emission measurement from Paint 2, Linoleum and Wood could be expressed as below in terms of the performance indices defined above, and the optimal signal intensity factors for this case were $\vec{\alpha}_{\text{true}}$ for [6 8 9] = [0.12 0.39 0.49] in the MRLS sense:

Algorithm 1 w/INIT: $ID_{\text{est1}} = [6 \ 7 \ 8 \ 9]$, $\vec{\alpha}_{\text{est1}} = [0.20_2 \ 0.17_7 \ 0.05_6 \ 0.09_9]$, $scr_1 = 90$.

Algorithm 2 w/LT: $ID_{\text{est2}} = [3 \ 6 \ 8 \ 9]$, $\vec{\alpha}_{\text{est2}} = [0.05_1 \ 0.17_1 \ 0.20 \ 0.26_8]$, $scr_2 = 90$.

After all, the overall performance results using the actual emission measurements from the mixtures are summarized in Table 4.

The case of the three-material mixture (i.e. [6 8 9] = Paint 2 + Linoleum + Wood, Measurement #4) without the long-term ES consideration ([6 8 9] with the initial ESs) showed the lowest performance with low success rates ($\leq 28\%$). The number of materials and the large change of ESs for Paint 2 appeared to contribute to the low performance. On the other hand, the adequate prediction close to the true shapes of the long-term ESs at a given later time via source models seemed to improve the separation/identification performance as demonstrated in Table 4. With Algorithm 2, the success rate was improved up to 76% from 26% before for the three-material mixture (i.e. [6 8 9], Measurement #4) and to 96% from 50% before for the Carpet and Linoleum mixture (i.e. [7 8], Measurement #5). The long-term ES for Carpet was also quite different from the initial one, so the proper prediction of the long-term ES for this material could improve the overall performance. For another two-material mixture (i.e. [8 9] = Linoleum + Wood, Measurement #6), however, there was a small difference between with and without the long-term ES consideration. The reason of this small difference may be due to the fact that the ES for Wood did not change much along the course of long-term emissions (belonging to the Type 1 material), and also the ES for Linoleum showed a small variation between the initial and the long-term ES even though this material belonged to the Type 2 material. These small shape changes in the corresponding ESs between the initial and long-term ones made no remarkable difference in the

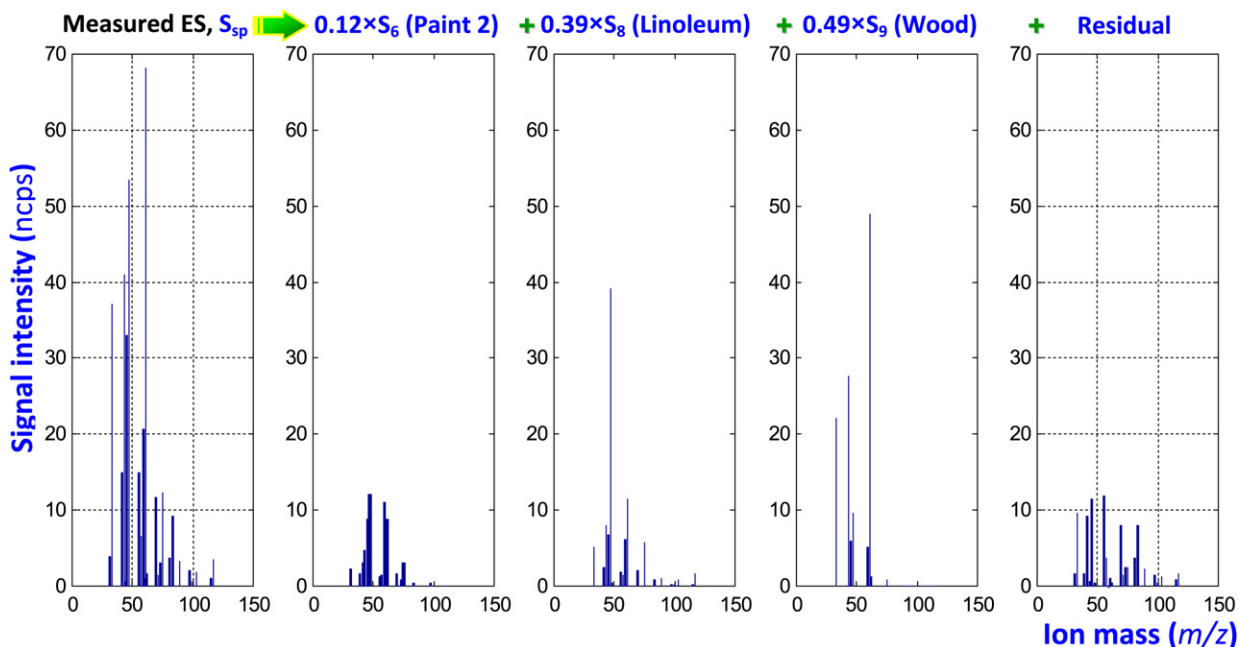


Fig. 10. Optimal separation results of the measured emission signature for the three-material mixture ([6 8 9]) in the sense of MRLS. The signal intensity of the measured emission signature for the mixture in ion mass $m/z = 33$ was compensated due to the abundance of O_2^+ ion ($m/z = 32$).

Table 4

Comparison of source ID performance by the ES predictions with 28-day short-term measurements for three mixture cases.

Material IDs with ground truths	ID _{est1} → α_{est1}^a	ID _{est2} → α_{est2}^a	Err1 ^b	Err2 ^b	Score1 (point)	Score2 (point)	SR1 (%)	SR2 (%)
[6 8 9] w/ INIT	[6 7 8 9] → [0.20 ₂ 0.17 ₇ 0.05 ₆ 0.09 ₉]	[6 7 8 9] → [0.06 ₇ 0.15 ₄ 0.19 ₄ 0.32 ₃]	0.42	0.26	25.20	23.00	28.00	26.00
[6 8 9] w/LT → [0.12 0.39 0.49]	[3 6] → [0.04 ₀ 0.38 ₄]	[3 6 8 9] → [0.05 ₁ 0.17 ₁ 0.20 ₀ 0.26 ₈]	0.40	0.28	27.20	66.00	30.00 (56.00)	76.00 (90.00) ^c
[7 8] w/INIT	[6 7 8] → [1.09 ₁ 0.53 ₅ 2.57 ₇]	[6 7 8] → [0.63 ₀ 0.48 ₁ 2.84 ₉]	0.95	0.76	45.00	44.60	50.00	50.00
[7 8] w/LT → [0.51 2.60]	[3 7 8] → [0.18 ₃ 0.34 ₃ 3.00 ₂]	[3 7 8] → [0.16 ₃ 0.46 ₀ 2.80 ₂]	0.61	0.38	86.00	83.60	96.00 (92.00)	96.00 (98.00)
[8 9] w/INIT	[3 6 8 9] → [0.05 ₇ 0.57 ₄ 2.03 ₅ 3.09 ₄]	[6 7 8 9] → [0.70 ₄ 0.13 ₂ 2.35 ₆ 3.08 ₁]	1.37	1.28	73.00	66.60	88.00	88.00
[8 9] w/LT → [2.50 4.25]	[1 3 8 9] → [0.05 ₈ 0.26 ₁ 2.87 ₅ 3.79 ₁]	[3 8 9] → [0.29 ₉ 2.43 ₁ 3.66 ₁]	0.63	0.72	72.00	74.20	88.00 (88.00)	88.00 (88.00)

[6 8 9] represents the three-material mixture consisting of Paint 2, Linoleum and Wood; [7 8] denotes the carpet and linoleum mixture; and [8 9] is the linoleum and wood mixture.

w/INIT: with the initial library of emission signatures; w/LT: with the consideration of long-term emissions.

The updated library of emission signatures at the 9-month period was predicted by using the power-law model.

^a To exemplify the form of the results from the two algorithms, these estimation results (material ID set and the corresponding signal intensity factor vector) were presented in the table, obtained when the algorithms were applied to the representative (i.e. by averaging the measured 50 samples) emission signature measured for each given material mixture. However, the three performance indices were calculated using the 50 individual samples measured for each mixture, following the definitions of the performance indices shown in Eq. (8).

^b 1: of Algorithm 1, 2: of Algorithm 2.

^c The values in the parenthesis were obtained by estimating the emission signatures with the full measurements.

consideration of long-term emissions for this case. For the three-material mixture, the source separation/identification performance was slightly decreased when compared with the ES estimation case using the full long-term emission measurements. However, for other two-material mixtures, the prediction approach with the short-term dataset showed a similar performance to the full measurement cases.

4. Summary and conclusions

The following conclusions were drawn from the modeling and experimental results of the present study.

- Among the building materials studied, two types of materials were observed and differentiated: (1) emission rates of major VOCs decreased relatively slowly over time (e.g. linoleum and wood, whose half-life time constant τ was >40 h), which were well represented by the power-law decay and mechanistic diffusion-based source models; and (2) emission rates of major VOCs decreased relatively fast over the early stage of emissions ($\tau < 7$ h), having a relatively fast variation in the corresponding material's emission signature, but the signature became stable at a later period (e.g. Carpet, Paint 2).
- The emission signatures representing individual building materials may change over time, but the long-term emission signatures for most of the building materials studied (if with a high enough signal intensity) appeared to be stable and consistent after a certain period of time mainly due to relatively steady emission rates of the measured composing compounds for a given material after that time.
- The long-term material emission signatures were predicted with a sufficient accuracy ($<6\%$ difference variance) by using empirical source models and a mechanistic diffusion model for individual compounds. Using the predicted instead of that of new materials considerably enhanced the performance of the source identification method developed previously.
- For the predictions of the long-term VOC emissions and the corresponding emission signatures for a given material, the power-law decay model is recommended because of its good representation of internal diffusion-controlled emissions and its computationally efficient merit. The mechanistic diffusion approach is also recommendable for this purpose, but is more complicated to use than the power-law model.

- The testing schedule generally used in the practice for predicting long-term emissions (i.e. Day 0–2, Day 7, Day 14 and Day 28) was found to be valid and practical also for the collection of material emission signatures to establish a library of initial emission signatures for building materials studied and to predict the corresponding long-term emission signatures at a given later time using the source models for the purpose of source identification. Because of its physical basis, the mechanistic diffusion model requires a shorter minimum period of testing for the prediction purpose.

Finding emission sources would help solve the associated indoor air quality problem effectively. This study shows that the emission decay of individual VOCs from building materials and hence the variation in material emission signatures can be predicted and used for enhancing emission source identification under laboratory conditions. (Several field tests have been already performed and showed the validity of the aforementioned approach under field conditions also, and the results will be published in a separate paper.) With additional information on interzonal airflow patterns, the new PTR-MS based source identification technique has the potential to find the sources of concern even when the sources are invisible or hidden behind/in the construction of buildings. For the use of indoor air quality estimation in a given real environment, emission rates and emission factors of the building materials used in the present study can be found elsewhere [24].

In the future research, it is recommended to apply an independent experimental approach to determine the control parameters in the mechanistic diffusion model [25,26], and use these measured parameters for the predictions of short-term and long-term emission signatures. Further field studies should also be performed to make the approach discussed in the present study a practical tool for indoor air quality remediation in actual indoor environments because of a higher number of emission sources, more complicated phenomena such as adsorption, desorption and interzonal airflow patterns. The approach for long-term emission change compensation may become invalid in reactive environments like an ozone-reaction dominant zone. In addition, for some passive or active emission sources, any stable emission signature may not exist. Moreover, if any material contains heavy VOCs as high-polluting compounds major for its emission signature, the measured signature from material mixtures containing the

material in an office environment may be distorted from the superposed emission signature due to different adsorption effects or not even measurable using the monitoring device due to heavy adsorption effect along the sampling pathway, making the approach invalid. If any material emits different VOCs having highly different relative rates of decay for quite a long time, the approach described here may not be applied. In this regard, a broader range of emission sources should be further studied, and unknown field effects should be investigated under field conditions like in an office building before this new approach is widely utilized in indoor environments.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.buildenv.2012.06.011>.

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